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GB 2213175 A GB 2193738 A WO 94/03706 A1  
US 4681686 A

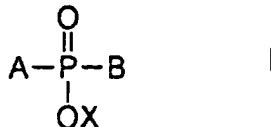
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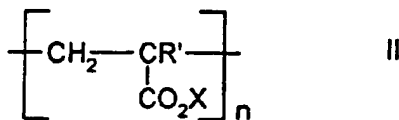
(54) Abstract Title

Phosphinopolycarboxylic acids comprising sulphonic acid groups and their use as inhibitors of barium sulphate scale

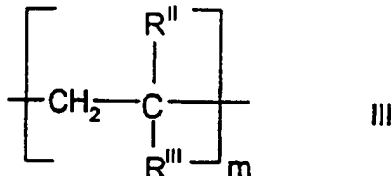
(57) A cotelomer has the formula I.



wherein A represents a random copolymeric residue comprising at least one unit of formula II



wherein R' represents a hydrogen atom or a methyl group, X represents a hydrogen atom, an alkali metal ion, an alkaline earth metal ion or an ammonium ion or an amine residue and n is an integer, together with at least one residue of formula III



wherein R'' represents a residue of formula (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>X wherein p has a value of 0 or 1, R''' represent a hydrogen atom or a methyl group with the proviso that when p is 0 R''' is a hydrogen atom, B represents a hydrogen atom or a residue A and the integers n and/or m in a residue A may be the same or different as the integers n and/or m in a residue B.

The cotelomers are used to inhibit the formation of barium sulphate scale, in particular in down-well oilfield applications.

GB 2 328 440 A

**DOCKET NUMBER:- 60114**

**PATENT APPLICATION**

**APPLICANT:- FMC CORPORATION (UK) LIMITED**

**TITLE:- SCALE INHIBITION PROCESS**

This invention relates to novel scale inhibitors useful *inter alia* to inhibit the formation of barium sulfate scale under severe scaling conditions such as are encountered in down-well oilfield applications.

The formation of scale formed predominantly or wholly of barium sulfate is a problem which is encountered in a variety of environments. One environment in which this problem arises is in the recovery of oil from undersea rock formations. Offshore oilfields may be injected with sea water so as to maintain oil production. Where this sea water mixes with existing subterranean formation water there is a possibility of barium sulfate precipitation. The precipitates can block the near well bore areas and production lines requiring removal of the precipitate or in extreme cases abandonment of the well.

To minimise the problem of scale formation a common practice in the industry is to force a scale inhibitor into the subterranean formation causing it to be adsorbed or precipitated onto the surface of the subterranean rocks. Over an extended period the inhibitor leaches back into the water and reduces or avoids the formation of barium sulfate scale. Such treatments are commonly termed "squeeze treatments". Squeeze treatment is a well established technique in the art as can be appreciated by reference to USP 4357248, USP 5060728, British Patent 2213516 and International Patent Application WO 94/03706.

A wide variety of inhibitors have been proposed for use in such squeeze treatments. They have enjoyed varying degrees of success in inhibiting the formations of scale. Recently some wells have encountered particularly severe scaling problems in which these known inhibitors have been ineffective or less effective. In these wells barium concentrations in excess of 400 ppm barium have been encountered in the formation waters. The pH of the waters may be more acidic than has previously been the norm often less than 5.0 and the concentration of total dissolved solids (TDS) in the water may be above 30,000ppm. All these factors may influence the effectiveness of the scale inhibitor. The known inhibitors may be less effective and may have to be used at higher concentrations and more frequently than was previously the case. There is therefore a need in the art for a barium sulfate scale inhibitor which is more effective especially under these severe scaling conditions.

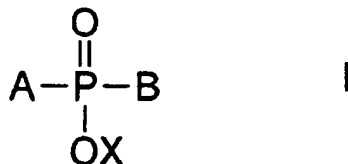
USP 4681686 discloses cotelomeric compounds which are phosphino poly (carboxylic acids) hereinafter for convenience PCA's and their use as scale inhibitors especially for salts derived from divalent metal ions such as calcium, magnesium, barium or strontium and anions such as sulfate, carbonate, hydroxide, phosphate or silicate. The patent also mentions the use of these inhibitors in a wide variety of applications including "down-well systems". This patent discloses a barium sulfate scale inhibition test which uses a solution containing 69.6 ppm  $Ba^{2+}$ .

USP 4898677 describes a process for inhibiting scale formation in water containing "significant" amounts of barium sulfate, which utilises an acrylic acid/vinyl sulfonic acid copolymer comprising 70 to 95% acrylic acid and 5 to 30% of vinyl sulfonic acid and/or its sodium salts and having a molecular weight of up to 90,000 as a scale inhibitor. Although this patent describes scale formation in down-hole systems the maximum barium sulphate concentration described is 375 ppm.

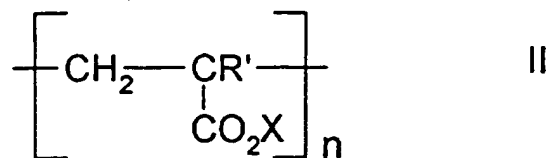
USP 4397002 describes the use of copolymers of acrylic acid and hydroxy ethyl acrylate to inhibit the formation of barium sulphate scale in waters comprising up to 700 ppm  $Ba^{2+}$  and at pH values as low as 4.7.

We have now discovered that phosphino poly (carboxylic acid) cotelomers comprising acrylic and/or methacrylic acid and vinyl sulfonic acid and/or (meth)allyl sulfonic acid or their salts are particularly effective in inhibiting the formation of barium sulfate scale especially in waters comprising at least 400 ppm  $Ba^{2+}$ . These phosphino poly (carboxylic acid) cotelomers are believed to be novel and constitute a further aspect of this invention.

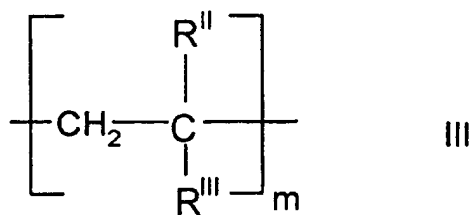
From one aspect this invention provides a method for inhibiting the formation of barium sulfate scale in an aqueous medium which comprises adding to that medium an effective quantity of a phosphino poly (carboxylic acid) cotelomer having the formula I



wherein A represents a random copolymeric residue comprising at least one unit having the formula II



wherein R' represents a hydrogen atom or a methyl group, X represents a hydrogen atom, an alkali metal ion, an alkaline earth metal ion or an ammonium ion or an amine residue and n is an integer, together with at least one unit having the formula III.



wherein R'' represents a residue having the formula  $(\text{CH}_2)_p\text{SO}_3\text{X}$  wherein p has a value of 0 or 1, R''' represents a hydrogen atom or a methyl group with the proviso that when p is 0 R''' is a hydrogen atom; X has its previous significance and m is an integer.

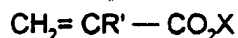
B represents a hydrogen atom or residue A and the integers n and m in a residue A may be the same or different as the integers n and m in a residue B; the ratio of n:m is in the range 5:1 to 25:1 and n and m have values such that the cotelomer has a weight average molecular weight ( $M_w$ ) of between 2,500 and 20,000, preferably between 3,000 and 10,000, and most preferably between 3,000 and 5,000; and a number average molecular weight ( $M_n$ ) of between 1,500 and 10,000, preferably between 1,500 and 5,000, and most preferably between 1,500 and 2,500.

The methods of this invention preferably utilise cotelomer having formula I wherein R' represents a hydrogen atom. These preferred cotelomers may be derived from acrylic acid.

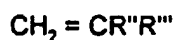
Cotelomers wherein p has a value of 0 may be derived from vinyl sulfonic acid (or more conveniently from a salt thereof such as sodium vinyl sulfonate). Cotelomers wherein p has a value of 1 and R' is a hydrogen may be derived from allyl sulfonic acid (or more

conveniently from a salt thereof such as sodium allyl sulfonate) or wherein R''' is a methyl group they may be derived from methallyl sulfonic acid (or more conveniently from a salt thereof such as sodium methallyl sulfonate).

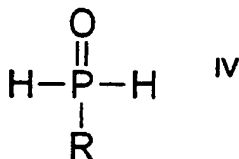
The cotelomers useful in the methods of this invention may be prepared using processes known in the art, for example those described in USP 4681686. Thus they may conveniently be prepared by the reaction of n moles of an acid having the formula



with m moles of a comonomer having the formula



wherein R', R'' and R''' have the significance defined above with one molar proportion of a telogen having the formula IV.



wherein R represents a residue OX and X has the significance defined above.

The reaction may be carried out in a solvent inert under the reaction conditions and in the presence of a reaction initiator as described in USP 2957931. Suitable reaction solvents are for instance, water, aqueous ethanol or dioxane. Suitable reaction initiators include materials which decompose under reaction conditions to yield free radicals. Examples of such materials are bisazoisobutyronitrile, organic peroxides such as benzoyl peroxide, methyl ethyl ketone peroxide, ditertiary butyl peroxide and monobutyl hydroperoxide, and oxidising agents such as hydrogen peroxide, sodium perborate and sodium persulfate.

The products of this process are obtained as solutions. These may be subjected to partial or complete evaporation under reduced pressure. The unpurified reaction products may be

used as the cotelomeric products in the method of the invention. The reaction products may also be purified. The purification procedure may be:

- (i) by evaporation of reaction solvent, dissolving the residue in water, washing with a water immiscible organic solvent e.g. ether and evaporation of the aqueous solution.
- (ii) by evaporation of reaction solvent, dissolving the residue in methanol and reprecipitation by addition of ether.

Salts of the compounds of formula I in which some or all of the acidic hydrogens in the compounds of formula I have been replaced by the cations derived from the salt forming bases hereinbefore defined, may be prepared by mixing an aqueous or alcoholic solution of the compound of formula I with an aqueous or alcoholic solution containing an amount of the requisite base in excess of, equal to or less than the stoichiometric requirement. The solvent may then be removed by evaporation. In many of the water-containing systems where inhibitors of this invention would prove useful, the water is sufficiently alkaline to effect neutralisation and only the phosphino poly (carboxylic acid) cotelomer produced by the processes described above need be added to the aqueous medium.

The ratio of the comonomers used in the reaction *i.e.* the ratio of the integers *n* and *m* will be selected so as to provide the ratio's required in the product. In the preferred embodiment the ratio of *n* : *m* is in the range 10:1 to 25:1.

The nature of the phosphino poly(carboxylic acid) cotelomers is also influenced by a number of other factors. In particular the ratio of the total molar proportion of comonomers (*i.e.* the sum of *n* and *m*) to the molar proportion of telogen having the formula IV. In general this ratio will be in the range 10:1 to 100:1 preferably 10:1 to 20:1.

The cotelomers of formula I will be added to the aqueous medium in a quantity which is effective in inhibiting the formation of barium sulfate scale. The cotelomers of this invention are surprisingly more effective than the generality of the class of cotelomers described in USP 4681686. In general the cotelomers of this invention will be used in a manner so as to provide a scale inhibiting amount to treat a particular system, this amount will vary with the aqueous system being treated. Generally the amount will be in the range of 0.1 to 500ppm. The squeeze treatment processes in which the methods of this invention find particular application, generally comprise a procedure involving the injection of a solution of the

inhibitor onto the subterranean rock formation, the adsorption of the inhibitor onto the surface of the rock and the gradual desorption of the inhibitor into the brines which are recovered from the well. The concentration of the inhibitor is most conveniently measured in this recovered brine produced when the well is producing oil. When the concentration of inhibitor falls below a preselected level the operator may elect to halt production and carry out a further squeeze treatment. Immediately after production is resumed the concentration of the inhibitor in the recovered brine may be relatively high. This concentration tends to fall rapidly to a plateau and then decrease slowly during operation as the inhibitor is desorbed from the rock. The amount of inhibitor used in the squeeze process will be sufficient to ensure that this plateau is at a level sufficient to reduce scale formation. The amount required will be determined empirically.

The inhibitor used in the methods of the invention may be used in conjunction with further scale inhibiting agents, e.g. a polymerised acrylic acid (or its salts), other phosphino-polycarboxylic acids (as described and claimed in GB 1428235) hydrolysed polyacrylonitrile, polymerised methacrylic acid and its salts, tannin, naphthalene sulfonic acid/formaldehyde condensation products, starch and its derivatives, cellulose, acrylic acid/lower alkyl hydroxyacrylate copolymers, e.g. those described in USP 4029577 styrene/maleic anhydride copolymers and sulfonated styrene homopolymers, e.g. those described in USP 4374733 and combinations thereof. Specific threshold agents, such as for example, 2-phosphonobutane-1,2,4-tricarboxylic acid, amino trimethylene phosphonic acid, diethylene triamine pentamethylene phosphonic acid, octamethylene tetraamino hexamethylene phosphonic acid, acetodiphosphonic acid, hydrolysed polymaleic anhydride and its salts, alkyl phosphonic acids, hydroxyphosphonoacetic acid, 1-aminoalkyl-1,1-diphosphonic acids and their salts, and alkali metal polyphosphates may also be used.

The inhibitors may also be used in combination with precipitating agents such as alkali metal orthophosphates, carbonate; oxygen scavengers such as alkali metal sulfites and hydrazine; sequestering agents such as nitrilotriacetic acid and its salts; antifoaming agents such as silicones, e.g. polydimethylsiloxanes, distearylsebacamide, distearyl adipamide and related products derived from ethylene oxide and/or propylene oxide condensations, in addition to fatty alcohols such as capryl alcohols and their ethylene oxide condensates and biocides; e.g. amines, quaternary ammonium compounds, chlorophenols, sulfur-containing compounds such as sulfones, methylene bis thiocyanates and carbamates, isothiazolones,



brominated propionamides, triazines, phosphonium compounds, glutaraldehyde and organometallic compound such as tributyl tin oxide.

The phosphino poly(carboxylic acid) scale inhibitors may also be used in combination with particular additives used in squeeze treatment processes in particular those additives known to promote adsorption of the inhibitor onto the rock. Examples of such additives include multi valent cations such as trivalent chromium, calcium, iron, titanium, zirconium, zinc and copper; and heat sensitive pH increasing compounds such as urea or derivatives thereof as described in WO 94/03706.

The molecular weight values quoted in the examples below were determined using a GPC method in which, a silica based separating agent was used with a solution of 0.003M sodium hydrogen orthophosphate and 0.007M sodium dihydrogen orthophosphate plus 0.14M sodium chloride as eluent. This was run at room temperature with 1mL/min flow rate and a 30 $\mu$ L injection volume of a 0.5% solution. Sodium polyacrylate standards were used to calibrate the column. All references to molecular weight of the cotelomers in this specification refer to weights determined using this method.

The invention is illustrated by the following examples:-

#### Example 1

Cotelomer of acrylic acid and sodium allyl sulfonate in the molar ratio 18.9:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 15.8:1.

A flask containing 25mL water was heated to reflux. To this flask was added (a) over 2 $\frac{1}{4}$  hours, 1.19g sodium persulfate dissolved in 10mL water, and (b) over 2 hours, 4.4g sodium hypophosphite, 54g acrylic acid and 22.8g sodium allyl sulfonate (25%) dissolved in 45mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 156.4g and solids content 41.9% was obtained which had a  $M_w$  3850 and  $M_n$  1900.

### Example 2

Cotelomer of acrylic acid and sodium allyl sulfonate in the molar ratio 15:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A flask containing 25mL water was heated to reflux. To this flask was added (a) over 2 $\frac{1}{4}$  hours, 1.19g sodium persulfate dissolved in 10mL water, and (b) over 2 hours, 4.4g sodium hypophosphite, 54g acrylic acid and 28.8g sodium allyl sulfonate (25%) dissolved in 44mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 160.0g and solids content 43.1% was obtained which had a  $M_w$  3900 and  $M_n$  1900.

### Example 3

Cotelomer of acrylic acid and sodium allyl sulfonate in the molar ratio 12.6:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 15.7:1.

A flask containing 50mL water was heated to reflux. To this flask was added (a) over 2 $\frac{1}{4}$  hours, 2.38g sodium persulfate dissolved in 20mL water, and (b) over 2 hours, 8.8g sodium hypophosphite, 104.7g acrylic acid and 66.1g sodium allyl sulfonate (25%) dissolved in 80mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 305.1g and solids content 41.6% was obtained which had a  $M_w$  3650 and  $M_n$  1800.

### Example 4

Cotelomer of acrylic acid and sodium allyl sulfonate in the molar ratio 10:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A flask containing 50mL water was heated to reflux. To this flask was added (a) over  $2\frac{1}{4}$  hours, 2.38g sodium persulfate dissolved in 20mL water, and (b) over 2 hours, 8.8g sodium hypophosphite, 104.7g acrylic acid and 83.8g sodium allyl sulfonate (25%) dissolved in 72.5mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 329.6g and solids content 43.8% was obtained which had a  $M_w$  3900 and  $M_n$  1810.

#### Example 5

Coteleromer of acrylic acid and sodium vinyl sulfonate in the molar ratio 10:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A flask containing 50mL water was heated to reflux. To this flask was added (a) over  $2\frac{1}{4}$  hours, 2.38g sodium persulfate dissolved in 20mL water, and (b) over 2 hours, 8.8g sodium hypophosphite, 104.7g acrylic acid and 75.7g sodium vinyl sulfonate (25%) dissolved in 72.5mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 321.6g and solids content 43.2% was obtained which had a  $M_w$  3180 and  $M_n$  1780.

#### Example 6

Coteleromer of acrylic acid and the sodium salt of 2-acrylamido-2-methylpropane sulfonate (AMPS) in the molar ratio 10:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A flask containing 50mL water was heated to reflux. To this flask was added (a) over  $2\frac{1}{4}$  hours, 2.38g sodium persulfate dissolved in 20mL water, (b) over 2 hours, 8.8g sodium hypophosphite dissolved in 120mL water, and (c) 104.7g acrylic acid and 66.4g AMPS (50%). The initiator addition was started 5 minutes before the monomers and finished 10

minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 346.2g and solids content 41.0% was obtained which had a  $M_w$  3700 and  $M_n$  1900.

#### Example 7

Copolymer of acrylic acid and the potassium salt of 3-sulfopropyl acrylate (SPAK) in the molar ratio 10:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A flask containing 50mL water was heated to reflux. To this flask was added (a) over  $2\frac{1}{4}$  hours, 2.38g sodium persulfate dissolved in 20mL water, and (b) over 2 hours, 8.8g sodium hypophosphite, 104.7g acrylic acid and 33.7g SPAK dissolved in 72.5mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 290.1g and solids content 50.8% was obtained which had a  $M_w$  3860 and  $M_n$  1840.

#### Example 8

Copolymer of acrylic acid and sodium styrene sulfonate in the molar ratio 10:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A solution of 5.25g sodium hypophosphite monohydrate was dissolved in 50mL water and heated to reflux. To this solution was added (a) over  $2\frac{1}{4}$  hours, 2.38g sodium persulfate dissolved in 20mL water, and (b) over 2 hours, 5.25g sodium hypophosphite monohydrate, 104.7g acrylic acid and 30g sodium styrene sulfonate dissolved in 72.5mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 282.5g and solids content 51.4% was obtained which had a  $M_w$  4280 and  $M_n$  1900.

### Example 9

Cotelomer of acrylic acid and the sodium salt of 2-acrylamido-2-methylpropane sulfonate (AMPS) in the molar ratio 3.5:1 respectively with sodium hypophosphite in the molar ratio of total monomers to sodium hypophosphite 16:1.

A flask containing 70mL water was heated to reflux. To this flask was added (a) over 2 $\frac{1}{4}$  hours, 2.08g sodium persulfate dissolved in 20mL water, (b) over 2 hours, 9.27g sodium hypophosphite monohydrate, 75.6g acrylic acid and 158.7g AMPS (50%) dissolved in 70mL water. The initiator addition was started 5 minutes before the monomers and finished 10 minutes after the monomer addition ends. On completion of these additions, the reaction mixture was heated for a further 2 hours at reflux.

A final product of weight 400.8g and solids content 41.3% was obtained which had a  $M_w$  3770 and  $M_n$  1980.

#### Barium Sulfate Capillary Tube Test

Sulfate and barium containing brines both buffered to pH 4.5 with sodium acetate/acetic acid buffer were preheated to 90°C by pumping through 2 x 1 metre long coiled 316 stainless steel tubes immersed in a hot water bath. A metre long coiled 316 stainless steel test capillary tube (1.1 mm ID), and was attached to the two preheat coils by a 316 stainless steel "T" piece which formed a mixing chamber for the brine solutions. A pressure transducer measured any change in pressure differential across the tube due to scale buildup within the capillary. This change in pressure was given on a digital readout and was also transmitted to a chart recorder to record the rate of change of pressure with time. The test was run until the additive failed to prevent further barium sulfate growth or for a period of 2 hours. The failure point in this test is when the pressure difference ( $\Delta P$ ) recorded by the pressure transducer reaches 1psi. The final test water analysis for this test is given below.

Water chemistry for the 80:20 Miller field barium sulfate capillary tube test

<i>Ion</i>	<i>Concentration</i>
barium	840 ppm
strontium	89 ppm
calcium	940 ppm
magnesium	366 ppm
potassium	1550 ppm
sodium	25184 ppm
sulfate	530 ppm
chloride	42114 ppm

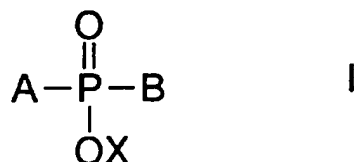
Test results presented as time taken to reach  $\Delta P = 1$  psi.

Example	Time/min
1	>120
2	>120
3	>120
4	91
5	>120
6	65
7	62
8	37
9	9

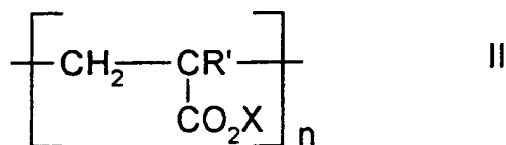
Examples 1 - 5 are examples of compounds having the formula 1. Examples 6 - 9 are comparative examples of other known scale inhibitors.

What we claim is:-

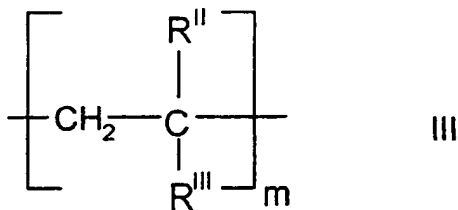
- 1) A method for inhibiting the formation of barium sulfate scale in an aqueous medium which comprises adding to that medium an effective quantity of a compound having the formula I



wherein A represents a random copolymeric residue comprising at least one unit having the formula II



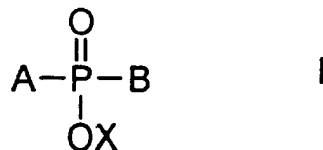
wherein R' represents a hydrogen atom or a methyl group, X represents a hydrogen atom, an alkali metal ion, an alkaline earth metal ion or an ammonium ion or an amine residue and n is an integer representing the number of repeat units, together with at least one residue having the formula III



wherein R<sup>II</sup> represents a residue having the formula (CH<sub>2</sub>)<sub>p</sub>SO<sub>3</sub>X wherein p has a value of 0 or 1, R<sup>III</sup> represents a hydrogen atom or a methyl group with the proviso that when p is 0 R<sup>III</sup> is a hydrogen atom; X has its previous significance and m is an integer.

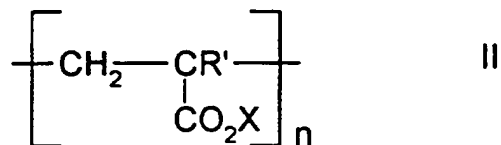
B represents a hydrogen atom or a residue A and the integers n and/or m in a residue A may be the same or different as the integers n and/or m in a residue B and the compound of formula I has a weight average molecular weight of from 2,500 to 20,000.

- 2) A method according to claim 1 characterised in that the compounds having the formula I has a weight average molecular weight ( $M_w$ ) in the range 3000 to 5000.
- 3) A method according to either of the preceeding claims characterised in that the compound of formula I has a number average molecular weight ( $M_n$ ) in the range 1500 to 2500.
- 4) A method according to any of the preceeding claims characterised in that in the formula II R' represents a hydrogen atom.
- 5) A method according to claim 4 characterised in that in the formula III p is 0.
- 6) A method according to claim 4 characterised in that in the formula III p has a value of 1.
- 7) A method according to any of the preceeding claims, characterised in that aqueous medium comprises from 0.1 to 500 ppm of a compound having the formula I.
- 8) A method according to any of the preceeding claims characterised in that an aqueous solution of the inhibitor of formula I is injected into a subterranean rock formation in the immediate vicinity of an oil well, the inhibitor is adsorbed onto the rock and desorbed into the recovered brines during oil production.
- 9) A method according to claim 8 characterised in that the concentration of barium ions in the formation water present in the oil well is in excess of 400 ppm.
- 10) A method according to either or claims 8 or 9 characterised in that the pH of the formation water is less than 5.0.
- 11) A compound having the formula I.

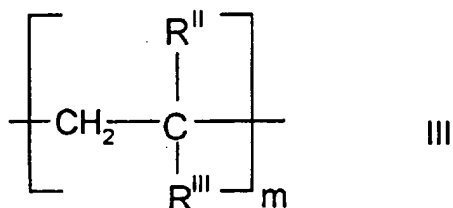




wherein A represents a random copolymeric residue comprising at least one unit having the formula II



wherein R' represents a hydrogen atom or a methyl group, X represents a hydrogen atom, an alkali metal ion, an alkaline earth metal ion or an ammonium ion or an amine residue and n is an integer representing the number of repeat units, together with at least one residue having the formula III



wherein R'' represents a residue having the formula  $(\text{CH}_2)_p\text{SO}_3\text{X}$  wherein p has a value of 0 or 1, R''' represent a hydrogen atom or a methyl group with the proviso that when p is 0 R''' is a hydrogen atom.

12) A compound according to claim 11 characterised in that R' represents a hydrogen atom.

13) A compound according to either of claims 11 or 12 characterised in that p has a value of 0.

14) A compound according to either of claims 12 or 13 characterised in that p has a value of 1.

15) A compound according to any of claims 11 to 14 having a weight average molecular weight of from 3000 to 5000.

- 16) A compound according to any of claims 12 to 16 having a number average molecular weight of from 1500 to 2500.



The  
Patent  
Office

Application No: GB 9717634.1  
Claims searched: 1 to 16

Examiner: Miss M M Kelman  
Date of search: 19 November 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C3P PHG, E1F FPE

Int Cl (Ed.6): C08F 2/38; E21B 37/06

Other: EDOC, JAPIO, WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 2213175 A ALBRIGHT & WILSON see the claims and page 5, lines 1 to 4	8,9,10
Y	GB 2193738 A NALCO see the claims	8,10
Y	WO 94/03706 A1 MOBIL OIL see pages 1 to 5	8,9,10
X,Y	US 4681686 A RICHARDSON <u>et al</u> see the claims and Examples 1 and 14	X:1 to 7,11 to 16 Y:8,9,10

X Document indicating lack of novelty or inventive step  
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.  
P Document published on or after the declared priority date but before the filing date of this invention.

E Patent document published on or after, but with priority date earlier than, the filing date of this application.